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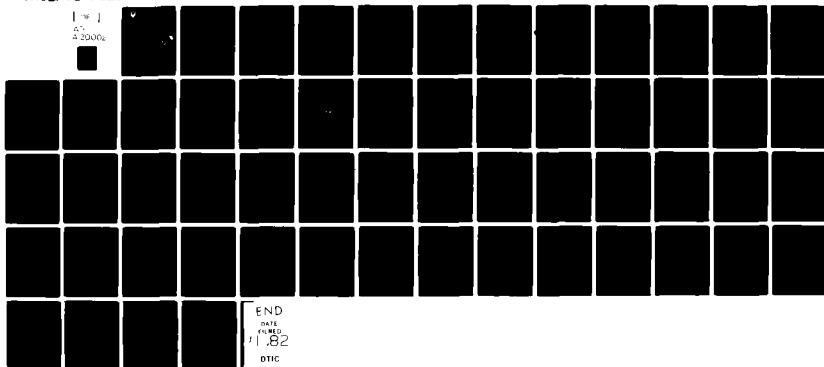
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STUDIES LEADING TO THE DEVELOPMENT OF HIGH-RATE LITHIUM SULFURY--ETC(U)
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Research and Development Technical Report

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Studies Leading to the Development of High-Rate
Lithium Sulfuryl Chloride Battery Technology

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September 1982

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This report details the investigations carried out in the second quarter of the program relating to Contract No. DAAK20-81-C-0420, during the period January 1, 1982 to March 31, 1982.		

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The overall aim of the program is an examination of the viability of an active electrolyte lithium-sulfuryl chloride battery system. The specific objectives are:

- o Quantify the stability of lithium in sulfuryl chloride solution.
- o Explore means to stabilize lithium in sulfuryl chloride.
- o Establish the limits of performance of carbon/teflon cathodes.

During the second quarter we:

- o Continued characterization of anode stability with respect to cell design and electrolyte composition.
- o Determined the voltage delay after storage as a function of electrolyte composition,
- o Characterized the performance at room temperatures of cells with and without performance additives.

We found that:

- o Positive grounding or floating of both electrodes with respect to the case enhance anode stability,
- o The bromine performance additive increases anode stability.
- o The bromine performance additive decrease voltage delay,
- o The bromine performance additive is superior to the chlorine performance additive in terms of delivered capacity.

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I. Introduction

Batteries built with an inorganic catholyte (e.g., thionyl chloride and sulfuryl chloride) are very attractive for military applications on the basis of their high demonstrated energy density, and high discharge rate capability when compared with organic electrolyte lithium cells. By far the greatest attention has been given to the lithium-thionyl chloride (Li/SOCl_2) system. Cells and batteries have been demonstrated with energy densities in excess of 600Wh/kg [1]. Less attention has been given to the development of lithium-sulfuryl chloride batteries possibly because of a somewhat lower theoretical energy density (1700 and 1500 Wh/kg for Li/SOCl_2 and $\text{Li/SO}_2\text{Cl}_2$ respectively).

Despite the impressive levels of performance demonstrated with Li/SOCl_2 wide spread deployment has not yet occurred principally due to unresolved safety issues. One of the probable causes for explosion of Li/SOCl_2 cells during overheating either as a result of short circuiting or an external heat source is the reaction between lithium and sulfur [2], which is formed by cell discharge according to the discharge reaction [3]



In this regard $\text{Li/SO}_2\text{Cl}_2$ may be a fundamentally safer system as no sulfur is formed in the discharge reaction [4].



Development of potentially safer $\text{Li/SO}_2\text{Cl}_2$ cells for military applications will require the demonstration of cells with a long shelf life and performance which at least approaches that of Li/SOCl_2 . The former requirement is principally a function of controlling the rate of lithium corrosion. The latter requirement entails optimization of the anode with respect to voltage delay and the cathode with respect to voltage and capacity in the range of 1 to 20 mA/cm² at temperatures down to -40°C.

The scope of the present contract encompasses investigation and improvements of both anode stability and electrode performance. Work in the second quarter, described in this report, has focused on demonstrating acceptable rates of anode corrosion and reducing voltage delay to acceptable levels by the use of proprietary additives.

II. Lithium Corrosion and Passive Film Formation in Sulfuryl Chloride

Work carried out in the first quarter established that

- The intrinsic corrosion rate of lithium in 1.5M $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$ as measured in ampule experiments is less than 1 mil per year (mpy).
- As has been previously observed in thionyl chloride [5,6] the passive film is disrupted by the passage of current and will result in reduced capacity in long term intermittent use.
- Measured in cell corrosion rates are at least an order of magnitude higher than those observed in ampule experiments.

Work this quarter has focused on characterizing the behavior of the lithium anode when the proprietary Gould bromine additive is used. Experiments have been carried out on cells and in ampules using both complex plane impedance and microcalorimetry as described in the first quarterly report.

II.1 Lithium Corrosion Studies

Previous corrosion studies described in the first quarterly report were carried out using a negative grounded cell design and a stainless steel case. Although electrolyte purification was found to decrease the rate of in-cell lithium corrosion the rate was still unacceptably high.

The cell design tested in the first quarter may not be optimum with respect to lithium stability. First, stainless may be attacked by the electrolyte, possibly leading to the formation of soluble heavy metal products which may plate out on the lithium. This could form a local cell and increase lithium corrosion. Secondly, it is unclear what the optimum electrode grounding choice is with respect to cell shelf life. Finally the studies were

not carried out with performance additives which may impact lithium stability in an unforeseen way.

The design of the three cells tested this month are summarized in Table 1. In cells 2 and 3 where the negative electrode floats with respect to the case of electrode were made by pressing 2 0.01 inch lithium foils to both faces of a 0.002" Ni foil. In the case of cell 1 the negative electrode was fabricated by pressure bonding a 0.01 inch lithium foil to the nickel can.

Calorimetric heat generation, corrosion and film resistance data for the three cells are summarized in Table 2. Although none of the cells demonstrated an acceptable rate of corrosion it does appear that floating the negative electrode with respect to the case (cells 2 and 3) leads to a lower corrosion rate than negative grounding. For cell 3 the rate of corrosion is exponentially decreasing with time as shown in Figure 1.

All the cells summarized in Table 1 developed leaks at the tin solder joint between the feedthrough eyelet and the case. The leakage precluded longer term testing and may have lead to an increase in the apparent corrosion rate as a result of

- Corrosion heat due to electrolyte attack on the solder and case material. To assess this an empty cell case was filled with electrolyte and its heat generation measured. 24 hours after construction the empty cell case was generating 241 μ W of heat. Thus as much as 40% of the heat ascribed to anode corrosion could arise from a secondary corrosion process.
- If soluble heavy metal products arise from secondary corrosion processes they would be expected to plate out on the anode and increase anode corrosion through the formation of a local cell.

Previously we have reported acceptable levels of anode corrosion (1mpy) in pure $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$ electrolyte in ampule experiments where possible cell impurities were eliminated. This month a further ampule test was carried with electrolyte containing the Gould bromine additive. As shown

Table 1

Design Characteristics of 1-inch Diameter Cells
for Anode Stability Testing

- 200 Ni case
- Glass to metal feedthrough
- $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$ electrolyte
- Bromine Additive
- 90% Shawinigan Black, 10% PTFE cathode
- 0.005 inch glass mat separator

Cell No.	Anode Area (cm^2)	Grounding
1	1.27	Negative
2	2.50	Floating
3	2.50	Positive

Table 2
Calorimetric and AC Impedance Data for Li/SO₂Cl₂ Cells

Time	Cell #1 Negative Grounded			Cell #2 Both Electrodes Floating			Cell #3 Positive Grounded		
	Heat Generation ($\mu\text{W}/\text{cm}^2$)	Corrosion Rate (mpy)	Resistance Film (Ω)	Heat Generation ($\mu\text{W}/\text{cm}^2$)	Corrosion Rate (mpy)	Resistance Film (Ω)	Heat Generation ($\mu\text{W}/\text{cm}^2$)	Corrosion Rate (mpy)	Resistance Film (Ω)
25	1470	562	22	1134	453	41	554	218	57
45	1050	420	38	785	314	89	381	153	80
70	790	316	-	-	-	-	209	83	-
140	162	56	-	-	-	-	78	31	-

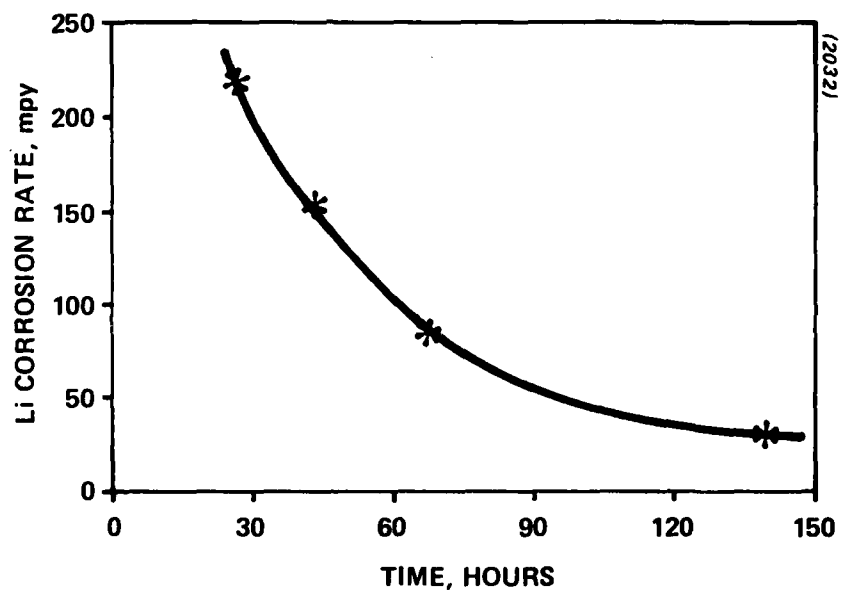


Figure 1 Lithium Corrosion Data in Sulfuryl Chloride
* 1 in Diameter cell with a Ni case
* 1.5M $\text{LiAlCl}_4\text{Br}/\text{SO}_2\text{Cl}_2$ Electrolyte
* Positive Grounded

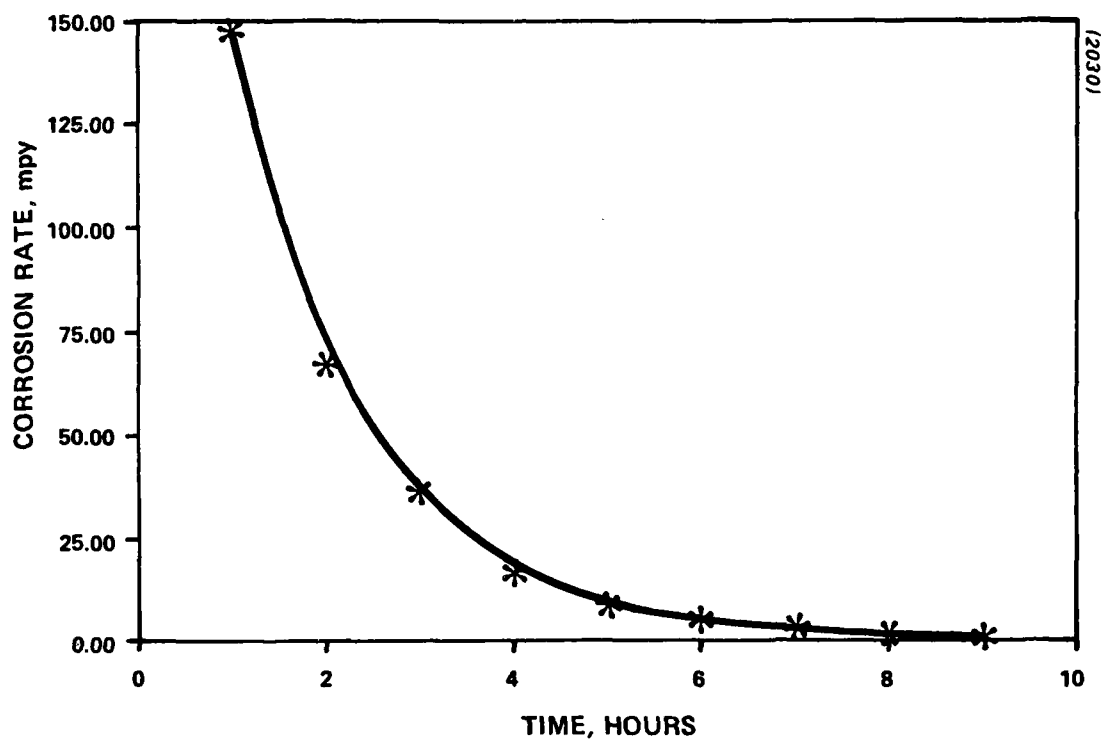


Figure 2 Lithium Corrosion Rate in a Glass Ampule at 25C Ampule Contains 3.3cm² of Lithium and 1.5M Lithium Tetrachloroaluminate in Sulfuryl Chloride with the Gould Performance Additive.

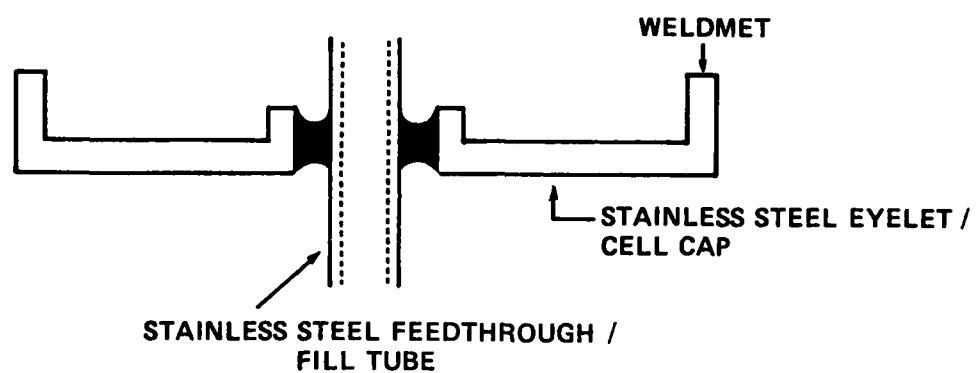
in Figure 2 with the additive the corrosion rate of lithium falls to zero within 9 hours. This is remarkably better than the cell data and a much lower corrosion rate than we previously reported for lithium corrosion in sulfuryl chloride electrolyte without bromine. As will be discussed in the section on voltage delay this result is in qualitative agreement with our finding that the additive reduces delay.

The above results indicate a strong materials/purity effect on the shelf life of cells. The immediate challenge is to translate ampule results into real cells. The obvious weakness of the present cell design is the need to use solder to join the feed through eyelet to the case. A new feedthrough has been designed (shown in Figure 3) which combines the cell lid with a glass to metal seal. This design eliminates the need for solder and only TIG welding will be required to seal the cell.

The metal eyelet parts of feedthrough shown in Figure 3 have been fabricated. The eyelets have been sent to a seal manufacturer with completed part delivery scheduled by the end of June. The complete cell cap/feedthrough assemblies will be used to construct flat cells, AA, D, and DD cells. Cases for these cells have been ordered and the flat, D and DD sizes received. We are confident that these steps will lead to the demonstration of an acceptable lithium corrosion rate in a real cell.

II.2. Cell Voltage Delay

Our efforts this quarter focused on the effects of the bromide additive on voltage delay. In the previous quarter, cells using 1.5M $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$ were found to exhibit an unacceptable amount of voltage delay after 48 hours at 60°C and in all cells stored for seven days as seen in Figures 4 and 5. This problem is reduced by replacing 0.5 moles of LiAlCl_4 with 0.5 moles of LiAlCl_3Br per liter. The results in Table 3 and Figures 6 and 7 clearly show a reduction in voltage delay for cells employing the bromine additive.



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Figure 3 Design of Solderless Feedthrough/fill tube/Cell Cap

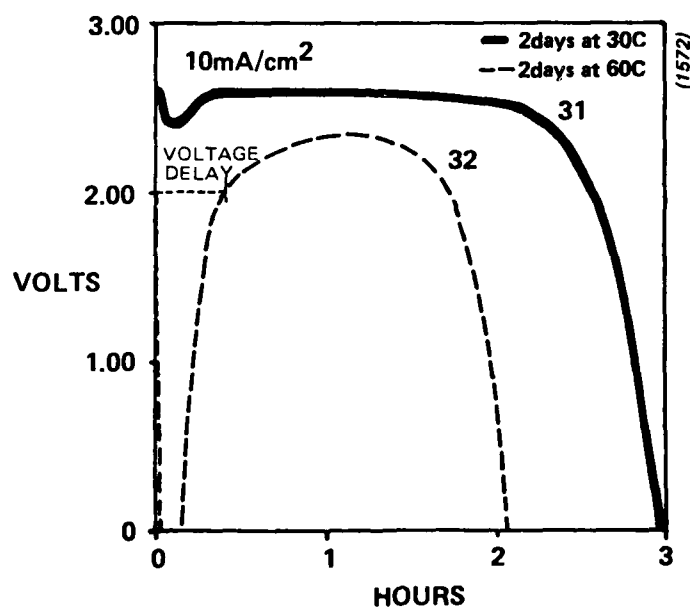


Figure 4 Discharge Curves showing Voltage Delay after two days storage

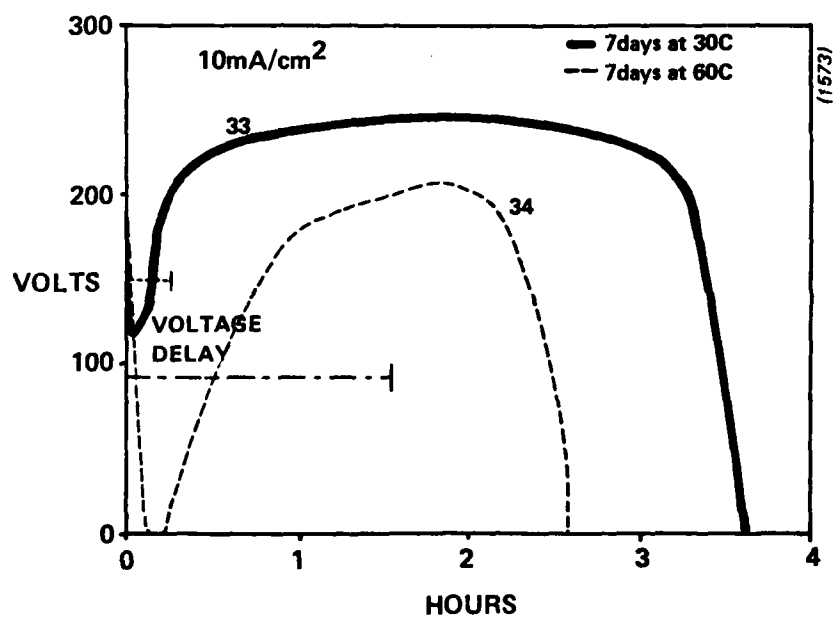


Figure 5 Discharge Curves showing Voltage Delay after Seven days storage

Table 3

Voltage Delay and Total Watt-hours Out of Baseline Cells
vs. Bromide Additive Cells

Time of					
Cell #	Temp(°C)	Storage (days)	Voltage Delay (h)	Watt-hours out	
31	30	2	-	1.00	
32	60	2	0.4	0.44	
33	30	7	0.25	0.54	
34	60	7	0.90	0.43	
<hr/>					
Bromine	11B	25	7	-	1.15
cells	13B	40	7	7.5	1.00
14B	60	7	11.5	2.99	

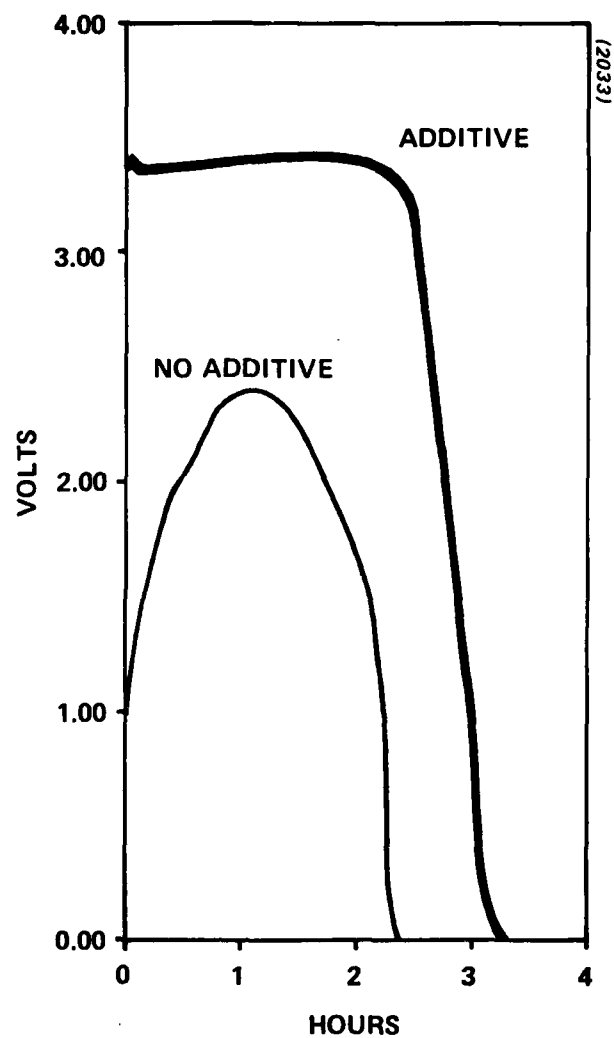


Figure 6 Discharge Curves of Li/SO₂Cl₂ 2in diameter
Test Cells stored at 25C for 2 days

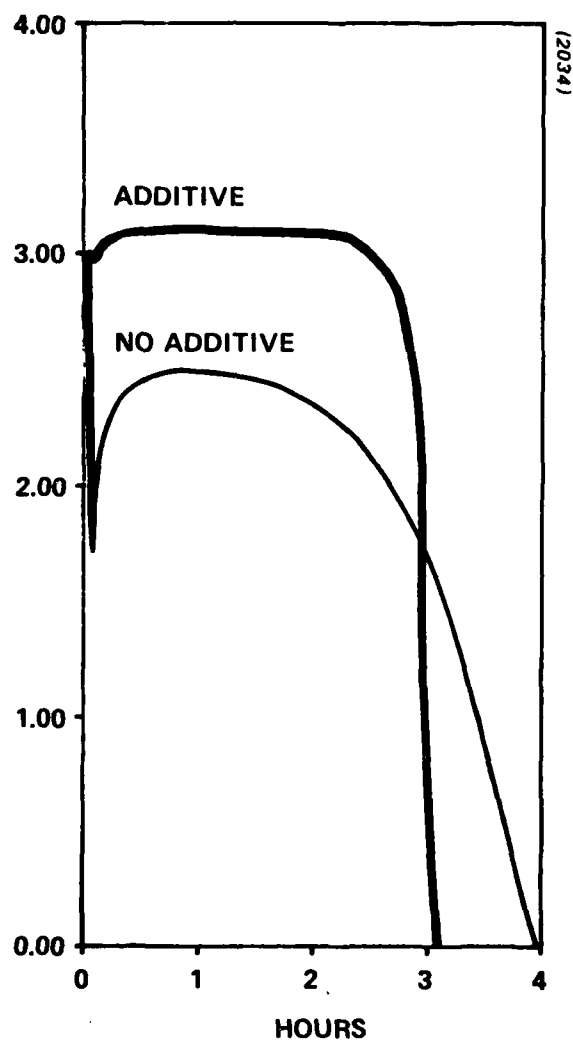


Figure 7 Discharge Curves of Li/SO₂Cl₂ 2 in diameter
Test Cells stored at 60C for 2 days

Additional testing of the bromine additive indicates that some voltage delay does occur at high temperatures after seven days of storage, but the initial voltage and the severity of the drop in voltage is considerably less as seen in Figures 7 and 8 than in cells without the additive. The discharge curves indicate a 5-7 minute voltage delay after 40°C and 60°C, but the voltage of neither of cells drops below 1.5 volts whereas in cells without the bromine additive cell voltage falls below zero on the application of current.

These results prompted the following investigation. A 2³ factorial experiment was designed to determine the effect the bromine addition has on cell performance. The effects of temperature and time of storage will also be determined as well as any interaction.

The experiment is as follows

Cell #		A	B	C	
1A	1	-	-	-	Factors:
2A	a	+	-	-	A. Temperature - 25°C
3A	b	-	+	-	+ 60°C
4A	ab	+	+	-	B. Additive - no additive
5A	c	-	-	+	+ additive
6A	ab	+	-	+	C. Storage Time - 2 days
7A	bc	-	+	+	- 7 days
8A	abc	+	+	+	

data accumulated will be cell capacity
total watt-hours and the voltage delay
 $i = 10\text{mA/cm}^2$

The test cell design used in this experiment is illustrated in Figure 9. The results to date as seen in Table 4 demonstrate the higher total watt-hours in cells stored with the bromine additive. More important though is the

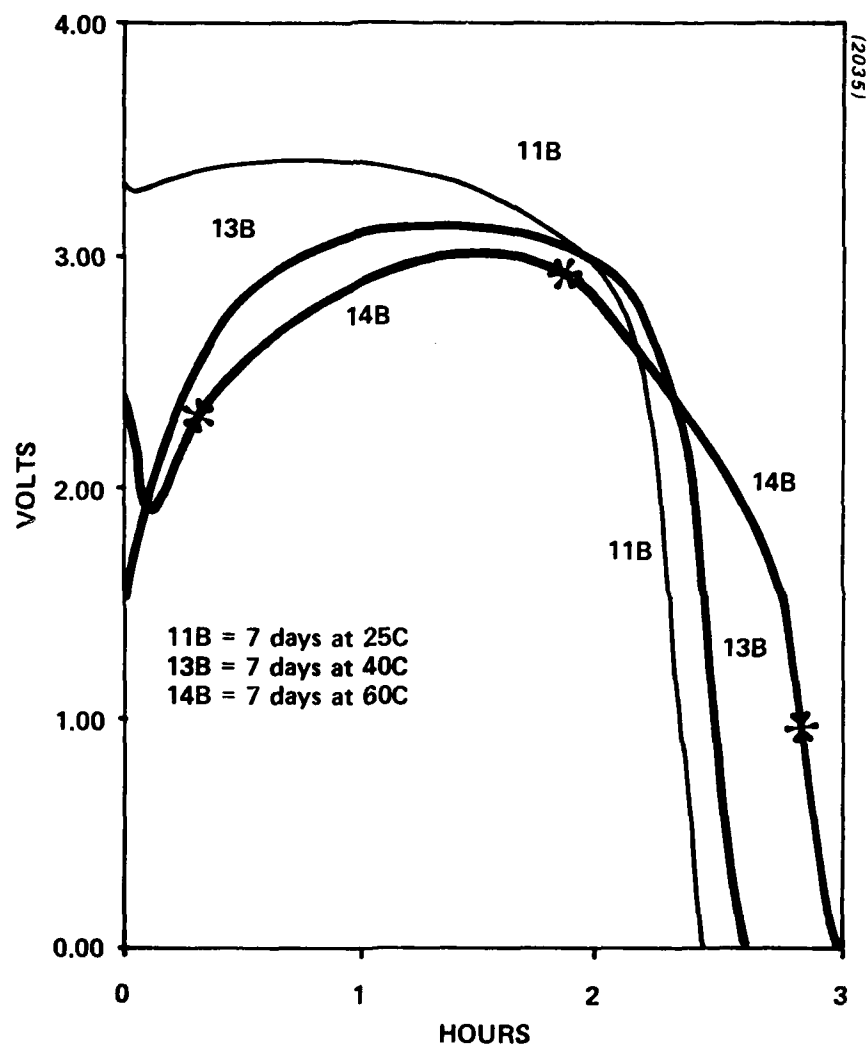


Figure 8 Discharge Curves of 11B, 13B, 14B (at 10mA/cm²)
with LiAlBrCl₃

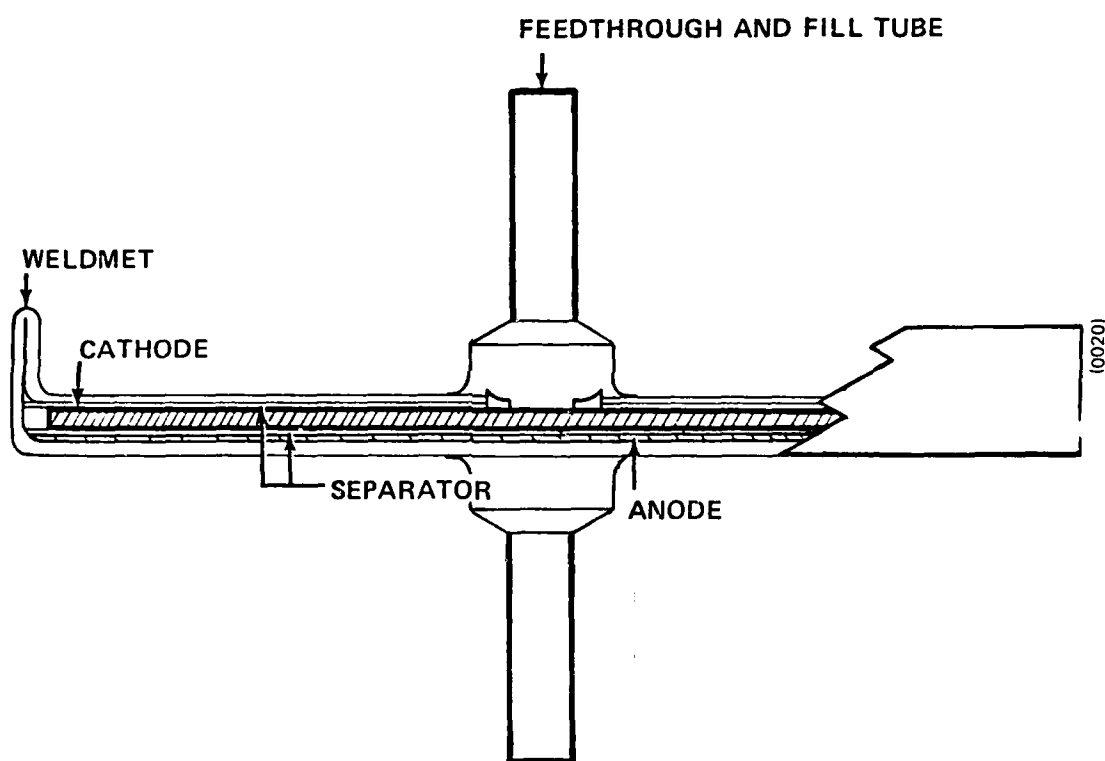


Figure 9 Schematic Cross Section and Description of 50mm diameter Cell used in $\text{Li}/\text{SO}_2\text{Cl}_2$ Studies

CATHODE: 90/10 Shawinigan Black/PTFE 0.35g pressed onto expanded Ni screen

ANODE: 20mil Lithium foil pressed onto expanded Ni screen

SEPARATOR: 5 mil Manniinglas

INSULATOR: 10 mil Telfon sheet

Table 4

Voltage Delay and Total Watt-hours Out from 2^3 Factorial Experiment

	Voltage Delay (h)	Total Watt-hours Out
- - - 1A	0.0	1.59
	0.1	1.18
	0.16	0.72
+ - - 2A	0.1	0.92
	0.75	1.17
	0.07	1.04
- + - 3A	0.0	1.42
	0.0	1.05
+ + - 4A	0.0	1.42
	0.0	0.97
	0.0	0.97
- - + 5A	1.54	0.69
+ - + 6A	0.9	0.78
- + + 7A	0.0	0.89
	0.0	1.27
+ + + 8A	0.12	1.02

lack of voltage delay in most of these cells. Voltage delay present in these cells lasted for no more than 5-7 minutes.

The mechanism by which voltage delay is reduced by the bromine additive is not fully characterized, but studies are underway to determine changes in the protective film caused by the bromine additive. Two mechanisms by which the bromine additive may affect the protective film are, inhibition of film growth resulting in a thinner film, and incorporation of impurities in the LiCl film as Dey [7] has suggested.

By having a thinner film, the voltage delay would be shorter since breakdown of the protective film and subsequent voltage rise would take less time. But, if indeed the film is thinner, is it as protective against corrosion? In cells discharged at $10\text{mA}/\text{cm}^2$ after 7 days storage the capacity is 37% less than cells immediately filled and discharged. If this loss of capacity is a product of a thinner film caused by the bromine additive, the additive may be unacceptable for active electrolyte batteries.

The other way the additive may affect film growth is by incorporating LiBr in the LiCl-LiCl lattice. By causing imperfections in the film, the film is not as tightly packed, more porous. The more porous film as suggested by Marikar [8] may have sufficient ion permibility that permits the anode reaction to proceed on initiation of cell discharge. At the same time the film must have a high degree of electrical resistivity to prevent continuous corrosion.

Scanning Electron Microscopy (S.E.M.) and energy dispersive x-ray analysis for the elements in the surface film are planned as two ways to monitor morphological and chemical changes in the protective film. Dey [7] and Marikar [8] have both used S.E.M as a technique for identifying morphological changes in the protective film. This method involves storing lithium foil in a sealed flask w/electrolyte and monitoring changes in the protective film.

Marikar [8] and Phillips [9] also have studied protective film growth using the in-situ technique of complex plane impedance. From this non-destructive technique, information on the film thickness can be ascertained. Using complex plane impedance we have determined film thickness for some of the treatments in the above 2^3 factorial experiment as seen in Table 5.

The data is incomplete so a statistical analysis can not be performed. No clear trends are immediately identifiable from the data.

Accumulation of the data on film thickness and the S.E.M. studies will help us to characterize and eventually control the growth of the film. Once control of the protective film is achieved, reduction or elimination of voltage delay will be achieved.

III. Cathode Studies

III.1 Baseline Data

In the area of cathode studies the assessment of the bromine additive and preliminary studies on Cl_2 addition were performed. In order to accurately assess the effect of these two additives baseline data for $\text{Li}/\text{SO}_2\text{Cl}_2$ cells with a supporting electrolyte of 1.5M LiAlCl_4 were first accumulated. The cells used were constructed as shown in Figure 9 and were run over a range of current densities ($1\text{--}20\text{mA}/\text{cm}^2$). From the baseline data in Table 6 the non-linearity of the capacity vs. current density is evident. This may be due to cathode swelling with wicking in of electrolyte and/or incomplete utilization of the cathode at higher current densities.

III.2. Cells with the Bromine Additive

Once the baseline data were accumulated testing of the bromide additive was initiated. The cells used for this study were identical to those used in

Table 5

Film Thickness
Data (in Angstroms)

	run 1	run 2
l	119	327
a	358	185
b	173	378
ab	202	218
c	203	264
ac	*	218
bc	347	350
abc	247	*

* data not available due to failure of fill tube to can solder joint

Table 6

Baseline Data for Li/SO₂Cl₂ Cells Using 1.5 M LiAlCl₄/SO₂Cl₂ Electrolyte

I(mA/cm ²)	Capacity (Ah)
1	N/A
2	0.888
	0.868
5	0.693
	0.660
10	0.459
	0.465
20	0.282
	0.270

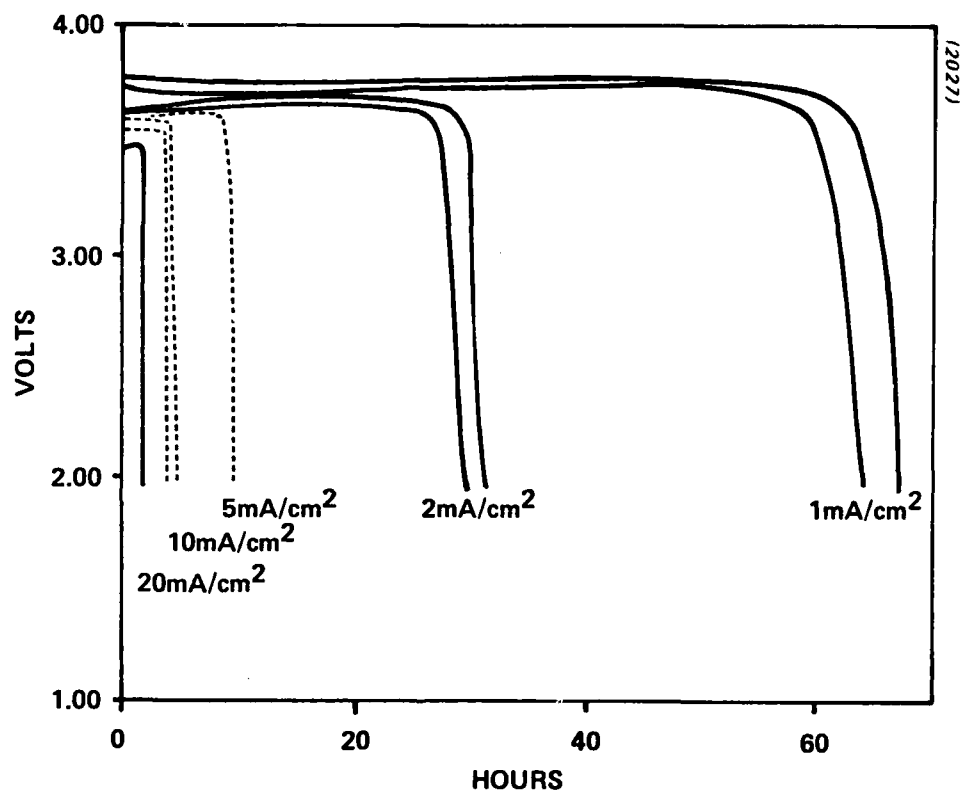


Figure 10 Discharge Curves of Li/SO₂Cl₂ Cells with LiAlBrCl₃ at a Range of Current Densities

Table 7

Baseline Data for $\text{Li}/\text{SO}_2\text{Cl}_2$ All With
 1.5M LiAlCl_4 vs. Data for LiSO_2Cl_2 Cells With
 1.0M LiAlCl_4 , $0.5\text{M LiAlCl}_3\text{Br}$

$i(\text{mA}/\text{cm}^2)$	Baseline Capacity (Ah)	Bromine Electrolyte Capacity (Ah)
1	N/A	.992
	N/A	.951
2	888	.925
	868	.985
5	.693	.729
	.660	
10	.459	0.618
	.463	0.600
20	0.282	0.522
	0.270	
25	< 0.1	0.212
		0.234
30	< 0.1	0.225
		0.234

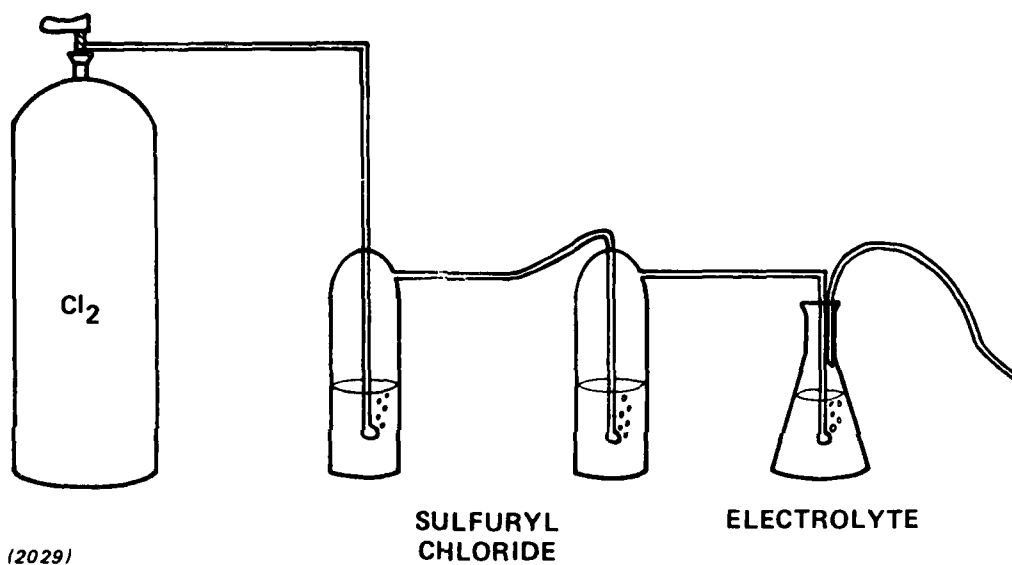


Figure 11 Cl_2 Gas Scrubbing Apparatus

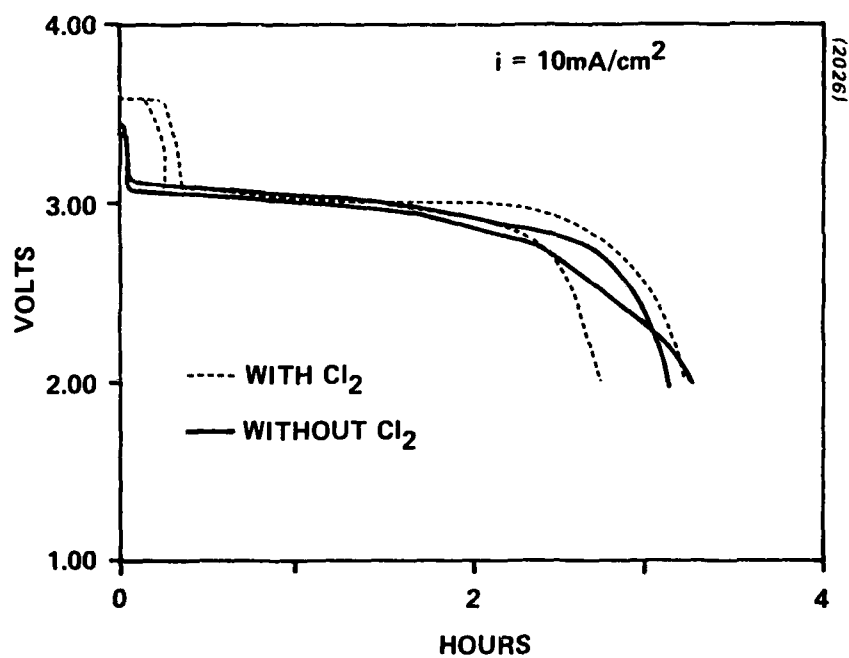


Figure 12 Discharge Curves of Li/SO₂Cl₂ Cells with and without Cl₂ Addition

the baseline study, but the electrolyte was $\text{SO}_2\text{Cl}_2/1.0\text{M LiAlCl}_4/0.5\text{M LiAlCl}_3\text{Br}$.

The discharge curves are seen in Figure 10, the capacity data is seen in Table 7, presented next to the baseline data. From the table it is quite evident that the bromine additive increases the capacity of the cell at all current densities. In addition, the additive results in a flatter, higher voltage discharge.

A further benefit of the Br_2 electrolyte is that it extends the usable range of current density of $\text{Li}/\text{SO}_2\text{Cl}_2$ cells. The original baseline data were taken up to current densities of $20\text{mA}/\text{cm}^2$. At $20\text{mA}/\text{cm}^2$ the capacity was only about 50% of theoretical, (0.450 Ah) at higher current densities the capacities are much less. In cells employing the bromine electrolyte the capacity is slightly above theoretical capacity (.450 Ah) and at $25\text{ mA}/\text{cm}^2$ and $30\text{ mA}/\text{cm}^2$ the capacity is 50% of the $20\text{mA}/\text{cm}^2$ capacity. This demonstrates that the bromine electrolyte allows a $20\text{mA}/\text{cm}^2$ discharge with no loss in capacity as compared to the theoretical capacity, and operation at current densities up to $30\text{mA}/\text{cm}^2$. In this range of current densities cells with the additive deliver at least twice the capacity of cells without the additive.

III.3. Cells with Added Chlorine

Another additive considered for sulfuryl chloride is chlorine. Work by Liang (10) indicates that storage times of at least one year, using Cl_2 as an additive to SO_2Cl_2 , are attainable with only an 8% loss in capacity (some voltage delay is evident). In addition an increase in the operating voltage and capacity of cells filled and immediately discharged are higher than cells filled and run without Cl_2 .

The addition of Cl_2 was thus proposed for our system. Using a double gas scrubbing apparatus seen in Figure 11 chlorine was added to a $\text{SO}_2\text{Cl}_2/1.5\text{M LiAlCl}_4$ solution. The weight and volume change of the solution was used to

calculate a final Cl_2 concentration of 0.5 M. Cells of the type described in Figure 9 were filled and discharged at $10\text{mA}/\text{cm}^2$. Two cells filled with $\text{SO}_2\text{Cl}_2/1.0\text{MLiAlCl}_4/0.5\text{MLiAlBrCl}_3$ were discharged simultaneously with the Cl_2 cells. The discharge curves for these four cells are seen in Figure 12. Aside from the initial high plateau, the curves for the Cl_2 cells are comparable to cells run without an additive. Figure 13 shows three curves, one for each type of electrolyte, performed at $10\text{mA}/\text{cm}^2$. The curve for the Cl_2 additive cell is remarkably similar to the no additive cell, coincidentally the capacity is also identical. The bromine additive cell has a higher capacity and average discharge voltage.

IV. IRAD $\text{Li}/\text{SO}_2\text{Cl}_2$ Development

In addition to executing the contract work (DAAK20-81-C-0420) Gould is independently carrying out development of $\text{Li}/\text{SO}_2\text{Cl}_2$ systems for a variety of potential military application. The results of this work indicate that in addition to greater safety the system offers significant performance advantages over more mature systems such as Li/SO_2 and Li/SOCl_2 .

Gould strongly concurs with the Army decision to pursue the development of safer, higher performance $\text{Li}/\text{SO}_2\text{Cl}_2$. In support of the Army we are including with this report a description of our IRAD work to demonstrate the potential performance advantages of $\text{Li}/\text{SO}_2\text{Cl}_2$ power sources.

IV.1. Mechanism of Operation

The generally accepted discharge reaction for a $\text{Li}/\text{SO}_2\text{Cl}_2$ cell is



The basis of the advanced Gould technology is the addition of bromine to the electrolyte. This addition can occur either as molecular bromine or a

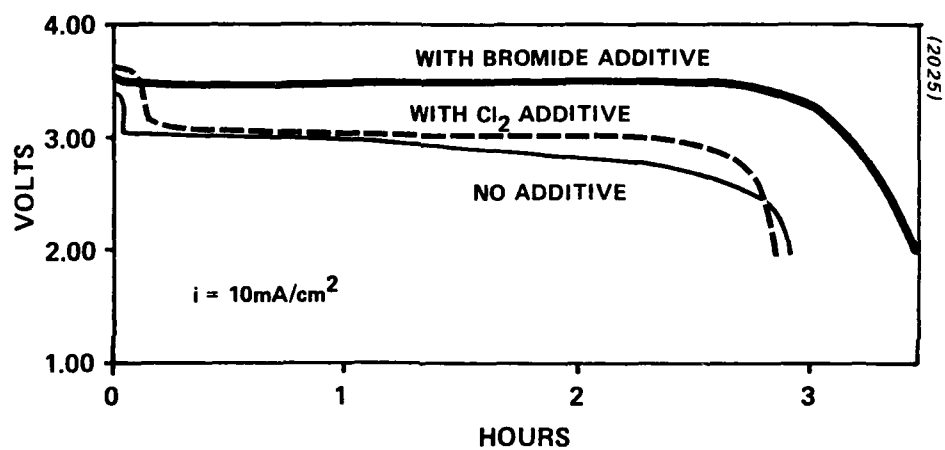


Figure 13 Discharge Curves of $\text{Li}/\text{SO}_2/\text{Cl}_2$ Cells with Bromide Additive, Cl_2 Addition, and No Additives

LiAlCl₃Br solute which forms bromine by the reaction.



We have found that reaction (2) proceeds to at least 80% completion using UV-visible spectroscopy.

Although bromide ion is chemically oxidized to bromine in SO₂Cl₂ we have obtained strong evidence summarized in Figure 14 that bromine is electrochemically reduced at a higher voltage vs. lithium than SO₂Cl₂ on carbon. The cyclic voltammograms in Figure 14 show two reduction peaks when bromine is present and only one lower voltage peak in its absence.

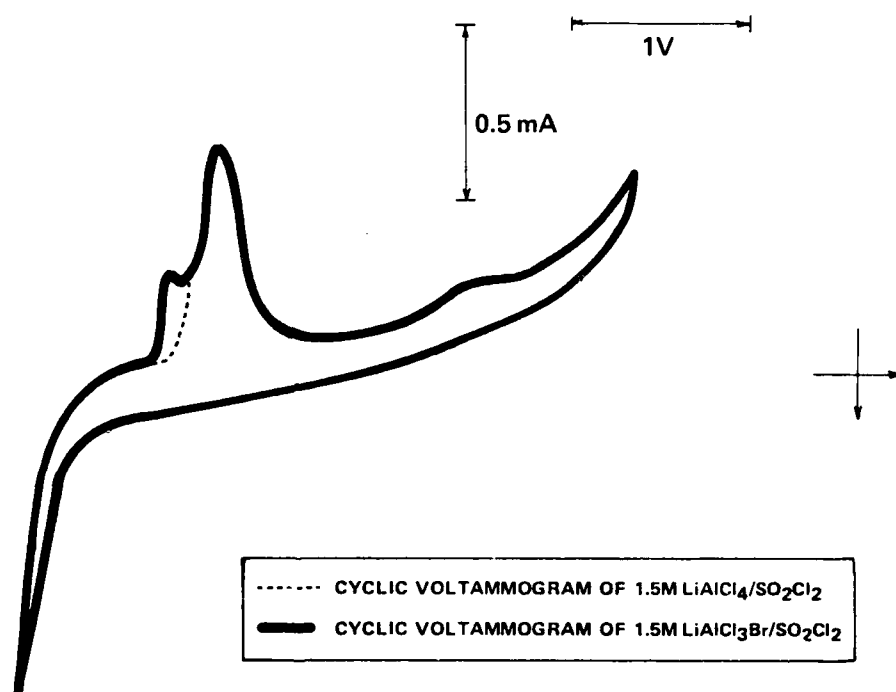
Based on these results it appears in a cell a cycle exists between electrochemically formed LiBr and chemically produced bromine and LiCl. This cycle may have two effects

- A high capacity at high current densities (e.g., >10mA/cm²) possibly because chemically produced LiCl is not as passivating as electrochemically produced LiCl.
- A greater high current density operating voltage or bromine is reduced at a lower over potential than SO₂Cl₂. As shown in Figure 15 cells with the additive are operable at current densities up to 50mA/cm².

Bromine appears to act as a catalyst of the second kind. That is it is consumed in the discharge reaction but reformed by a subsequent chemical reaction. As shown in Figure 16 the concentration of bromine is almost constant during discharge (the slight decrease in Figure 16 may be due to evaporation).

IV.2. Low Temperature Performance

One of the benefits of the bromine additive is that it enhances cell performance at low temperatures. In Figure 17 discharge data at 5mA/cm² and



(0789)

Figure 14 Cyclic Voltammogram on Glassy Carbon of 1.5M LiAlCl₃Br/SO₂Cl₂ and 1.5M LiAlCl₄/SO₂Cl₂

Scan Speed = 50 mV/sec

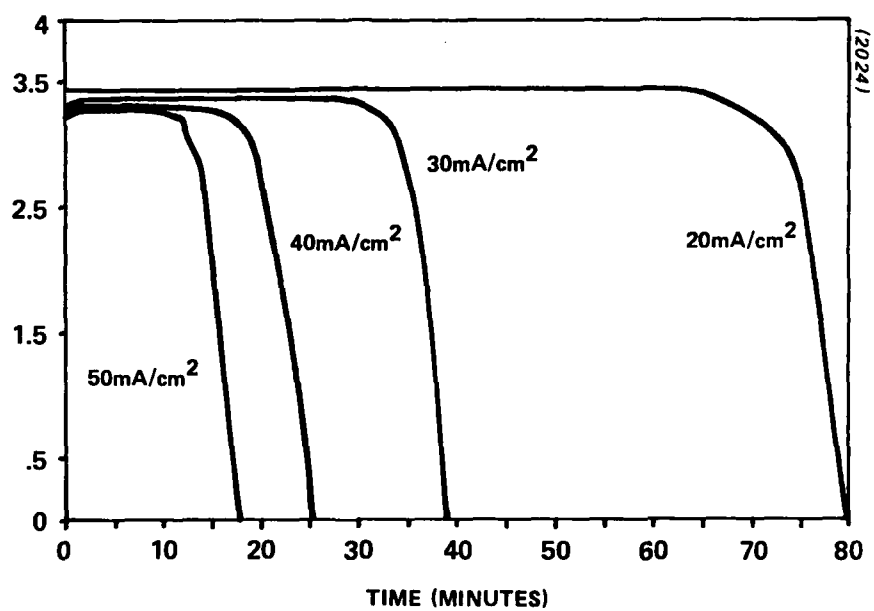


Figure 15 Discharge Behavior of Li/1.5M LiAlCl₃Br, SO₂Cl₂ Cells between 20 and 50 mA/cm²

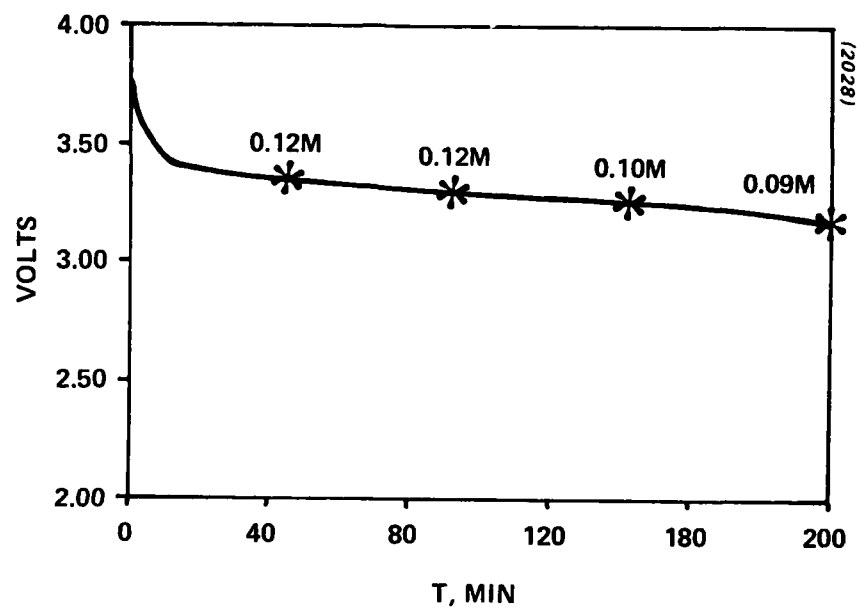


Figure 16 Lithium/Sulfuryl Chloride Bromine determination
UV/VIS spectroscopy at $10\text{mA}/\text{cm}^2$

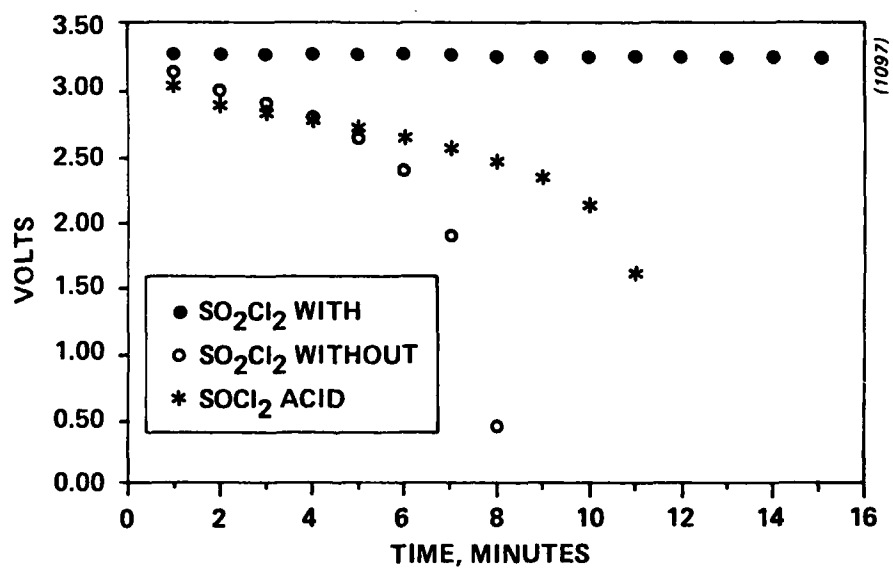


Figure 17 Low Temperature Discharge at $5\text{mA}/\text{cm}^2$ and -20°C

-20°C are given for Li/SO₂Cl₂ cells with and without bromine and acid electrolyte Li/SOCl₂. Only the cell with the bromine additive is operable at this temperature. In fact with the bromine additive cells are operable at substantially higher current densities. As shown in Figure 18 limited discharge is possible at current densities up to 20mA/cm² at -20°C.

IV.3. Simulated RPV Performance

One application we have explored for the Li/SO₂Cl₂ + bromine technology is its use as a power source for an electric drone. In this application the battery must meet the following requirements

- A 15 minute climb phase at approximately 10,000 W
- A 180 minute cruise phase at approximately 4,000 W

To assess candidate technologies for this application we have tested 7.5 cm diameter cells under a regime of 15 minutes at 40mA/cm² followed by full discharge at 15 mA/cm². All cells employed 2000 μm 90% Shawinigan Black, 10% PTFE positive current collectors.

In Figure 19 discharge data for the 40mA/cm² simulated climb phase are given for Li/SO₂Cl₂ + bromine and acid and neutral electrolyte Li/SOCl₂. Although all three systems operate the Li/SO₂Cl₂ + bromine cell clearly has the best voltage. In the subsequent simulated cruise phase shown in Figure 20 Li/SO₂Cl₂ + bromine has both a greater voltage and between 20 to 100% greater capacity.

IV.4. Underwater Target Simulation

A second possible application we have explored for the Li/SO₂Cl₂ + bromine system is its use in an underwater target for both propulsion and

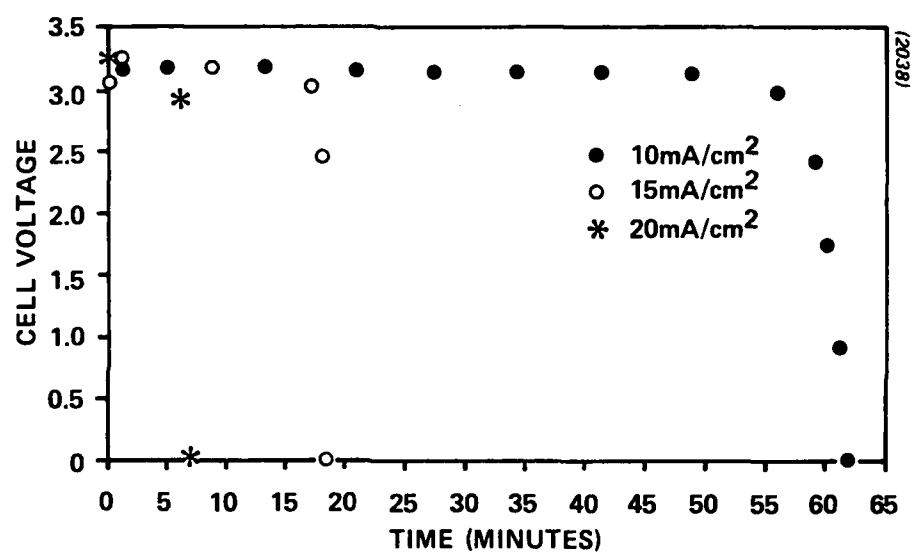


Figure 18 Discharge of Li/1.5M LiAlCl₃Br, SO₂Cl₂ at -20°C between 10 and 20 mA/cm²

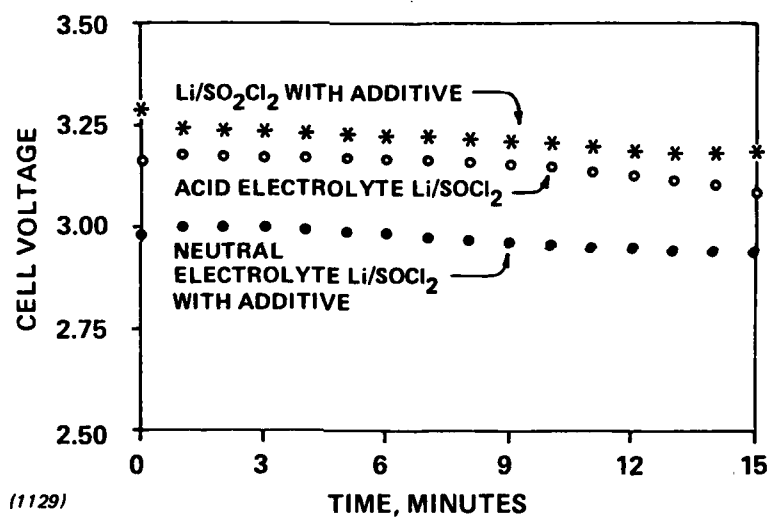
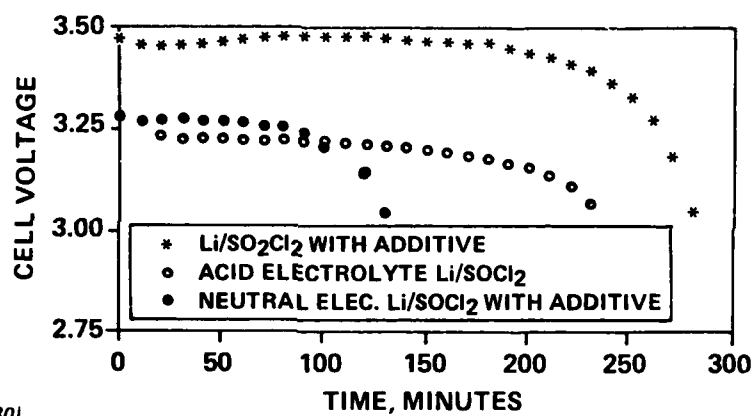


Figure 19 Discharge Data at 40mA/cm² 2.5mm 90%C, 10% PTFE Cathode, 0.05mm Anode, 7.5cm Ø Welded Cell



(1130)

Figure 20 Discharge Data at $15\text{mA}/\text{cm}^2$ after an initial $40\text{mA}/\text{cm}^2$
15 Minute Discharge. 2.5mm 90% C, 10% PTFE
Cathode, 0.05mm Anode, 7.5cm \varnothing Welded Cell

acoustic simulation. In this application a battery must be capable of

- A three hour discharge duration for propulsion
- During the last 90 minutes of discharge 200 msec. pulses every 2 sec. at 4 times the propulsion current.

In Figure 21 the performance of a Gould cell discharged at $15\text{mA}/\text{cm}^2$ for propulsion and $60\text{mA}/\text{cm}^2$ for acoustics is given. Also given are independently measured data for an Electrochem Industries $\text{Li}/\text{SO}_2\text{Cl}_2$ + chlorine cell under a similar discharge regime, but, at probably half the current density. The Gould cell at twice the current density provides approximately a 400mV voltage advantage for propulsion and 1.5V advantage for acoustics.

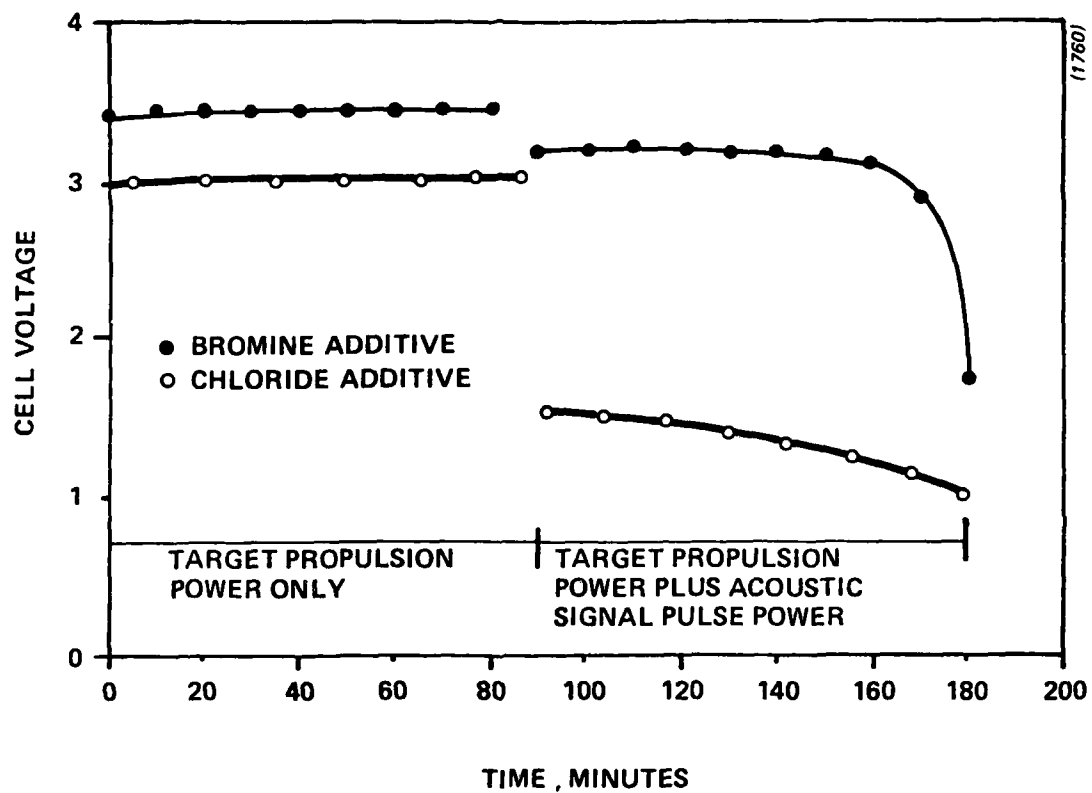


Figure 21 Lithium-Sulfuryl Chloride Cell performance comparison for Submarine Acoustic Target (EMAT) duty Cycle

V. Future Work

The principal goal of work during the third quarter will be to demonstrate a long shelf life cell. As mentioned in Section II advanced components for this have been ordered. Cells will be evaluated for both anode corrosion and voltage delay after storage.

Other planned contract activities during the third quarter include

- Parametric performance characterization of cells without additives, with the Gould additive and with added chlorine as a function of current density and temperature.
- Assess the effect of the chlorine additive on voltage delay after storage at room and elevated temperature.

In addition as part of our IRAD program we plan to initiate spectroscopic studies of cell safety during operation and reversal. The end of year goal of the contract and IRAD efforts is to establish the superior performance and potentially greater safety of $\text{Li/SO}_2\text{Cl}_2$ when compared with those systems presently in use by the Army.

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